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Catalytic Effectiveness Due to Mass Transfer Limitations in Triphase Catalysis by Polymer-Supported Quaternary Onium Salts

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Experimental results recently presented by Tomoi and Ford for the reactions of 1-bromooctane and of benzylbromide with aqueous sodium cyanide in triphase mixtures with polystyrene-supported benzyltri-n-butylphosphonium or benzyltrimethylammonium ions as phase transfer catalysts are considered. Mass transfer effects are shown to be in very good agreement with standard theory of porous catalysts. Intrinsic reaction rate constants and diffusion coefficients within the catalyst particles are estimated at various degrees of crosslinking of the polymeric matrix and for different solvents.

INTRODUCTION

Many features of phase-transfer catalysis make it attractive as a challenging technique and perhaps a competitive alternative route to the industrial preparation of several chemicals under very mild conditions. Phase-transfer catalysis is particularly suited whenever a reaction between a water-soluble reactant and a water-insoluble substrate is to be carried out (*1*). For industrial applications, however, a heterogeneous catalyst would be highly desirable in order to simplify catalyst separation and reuse and to easily operate with continuous processes.

Regen (*2*) first described effective phase-transfer catalysts linked to an insoluble polymeric matrix and suggested the name Triphase Catalysis. Although immobilized phase-transfer catalysts proved to be rather less active than the original soluble catalytic agents, a considerable effort has been made in very recent years in order to understand factors which control activity of polymer-supported catalysts (*3*).

However, some general factors common to any ion-exchange heterogeneous catalysis must be considered.

I. Hammett assumed the resin structure alters the environment of the transition state by imposing restraints upon it, which reduces its entropy (*4*). Consequently the reaction rate is lower with a more tightly knit structure of a more highly crosslinked resin (*5*). The same behavior, due to the loss of internal degrees of freedom suffered by the sorbed reactants in the formation of the transition state according to Eyring's theory (*6*), can be explained likewise, in terms of the limitations on the collision rate owing to the resin structure, through the lowering of the steric factor according to collision theory (*7*).

II. Helfferich (*8*) treated the pore liquid of the resin, where reaction occurs, as a homogeneous system in which the reactants are distributed between pore liquid and supernatant solution according to distribution coefficients. He emphasized the importance of the distribution coefficients, which may depend on the interactions among reactants, solvent, and polymeric matrix and therefore also on the degree of crosslinking.

III. Mass transfer phenomena must be taken into account whenever reaction rates are high enough that considerable concentration gradients are required in order to

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provide adequate material fluxes of reactants and reaction products. Mass transfer resistances on the boundary layer outside catalyst particles (film diffusion) as well as diffusive mass transfer resistances within the particles (particle diffusion) may be important factors affecting apparent reaction rates (*9*). Special attention must be given in case of triphase catalysis because both liquid phases must be in contact with the solid catalyst. A threshold dispersion level may exist, below which this contact is insufficient for the reaction to proceed.

Mass transfer and diffusion resistances in triphase catalysis have been forewarned by Regen (*10*) and Molinari *et al.* (*11*) and have been demonstrated by Tomoi and Ford (*12–14*).

Tomoi and Ford investigated the reactions of 1-bromooctane and of benzyl-bromide with aqueous sodium cyanide in triphase mixtures with polystyrene-supported benzyl tri-n-butylphosphonium or benzyltrimetylammonium ions as phase transfer catalysts. They focused their attention mainly on the following experimental parameters: mixing of the triphase system, catalyst particle size, degree of cross-linking of the polymeric support, and solvent. Evidence was presented that for the considered operating conditions the following processes could be rate limiting:

1. Mass transfer of organic substrate (1-bromooctane or benzyl bromide) from bulk organic phase to the surface of catalyst particles;
2. Diffusion of substrate through the polymeric matrix;
3. Intrinsic reactivity at the active sites.

They checked that reaction rates were first order with respect to substrate and linearly dependent on the amount of catalyst. Neither mass transfer of products nor ion exchange were discovered to affect reaction rates, although the latter might be important in some different operating conditions (*15*).

They discussed qualitatively the effects of each relevant factor. Some of those results, however, are still amenable to somewhat deeper analysis in order to present quantitative estimates of intrinsic properties for the considered catalytic systems. For this purpose well-established concepts pertinent to diffusive mass transfer in porous catalysts will be applied.

METHOD

Negligible film diffusion resistance. Mass transfer resistance through the boundary layer outside catalyst particles (film diffusion) is mainly dependent on flow dynamics, and may be made negligible by vigorously stirring the triphase system. If stirring is insufficient, film diffusion will be a simple series resistance to mass transfer. This will be discussed later. When film diffusion is negligible, the reactant concentration will be the same at the surface of the catalyst particles as in the bulk of liquid organic phase.

The molar rate of disappearance of substrate A (1-bromooctane or benzyl bromide) for a pseudo-first-order reaction in the triphase system may be written

$$\frac{-dN_A}{dt} = kM_c\lambda C_{As}\eta \qquad (1)$$

Neglecting film diffusion, the contribution to reaction at the exterior surface of the catalyst particles, and changes in the amount of reactant within the catalyst, the reaction rate for unit volume of organic phase is

$$\frac{-dC_A}{dt} = \frac{k\lambda M_c}{V_{org}} C_A\eta \qquad (2)$$

where the catalytic effectiveness η for spherical pellets is (*16*)

$$\eta = \frac{3\omega \coth(3\omega) - 1}{3\omega^2} \qquad (3)$$

and the Thiele modulus, ω, is

$$\omega = \frac{R}{3}\sqrt{\frac{k\lambda M_c}{V_{cat}D_s}} \qquad (4)$$

The pseudo-first-order reaction rate constant observed in case of negligible film resistance will be, from Eq. (2),

$$k_{obs} = \frac{k\lambda M_c}{V_{org}}\eta \qquad (5)$$

and substituting Eq. (3),

$$k_{obs} = \frac{3D_sV_{cat}}{R^2V_{org}}\left[R\sqrt{\frac{k\lambda M_c}{V_{cat}D_s}}\coth\left(R\sqrt{\frac{k\lambda M_c}{V_{cat}D_s}}\right) - 1\right] \qquad (5')$$

There are two unknown parameters in Eq. (5′), the effective diffusivity D_s of the reactant within the catalyst particle, and the product $k\lambda$ of intrinsic reaction rate and partition coefficient, which appear together and are indistinguishable from purely kinetic experiments. Estimates of both D_s and $k\lambda$ for each set of experimental k_{obs} can be obtained through a suitable nonlinear procedure. If a least squares criterion is adopted, the error sum of squares extended to the n experiments in the set,

$$S(D_s,k\lambda) = \sum_{i=1}^{n}\left\{k_{obs_i} - \frac{3D_sV_{cat_i}}{R_i^2V_{org_i}}\left[R_i\sqrt{\frac{k\lambda M_{c_i}}{V_{cat_i}D_s}}\coth\left(R_i\cdot\sqrt{\frac{k\lambda M_{c_i}}{V_{cat_i}D_s}}\right) - 1\right]\right\}^2 \qquad (6)$$

must be minimized with respect to D_s and $k\lambda$. Some well-established techniques are available for that purpose (*17*).

The potential of this method can be fully appreciated if a large amount of data is available for each set of experiments. If, as in the present case, only few data are supplied, estimates of the order of magnitude of the unknown parameters are the most ambitious achievable goal, and a simple shortcut graphical procedure is suggested.

Let us consider the well known log–log plot of catalytic effectiveness vs Thiele modulus as given by Eq. (3) and reported as the solid line in Fig. 1. Looking at Eq. (5) we may notice that $k_{obs}V_{org}/M_c$ is proportional to catalytic effectiveness, the proportionality constant being $k\lambda$. Analogously, looking at Eq. (4), $(R/3)\sqrt{M_c/V_{cat}}$ is proportional to the Thiele modulus and the proportionality factor is $\sqrt{D_s/(k\lambda)}$. Let us then construct a log–log plot of $k_{obs}V_{org}/M_c$ vs $(R/3)\sqrt{M_cV_{cat}}$. The experimental points will line up along a curve which, given a mere translation of log $(k\lambda)$ along the y axis and log $\sqrt{D_s/(k\lambda)}$ along the x axis, matches exactly with the effectiveness curve. Therefore, estimates of both D_s and $k\lambda$ can be derived by translating the row of the experimental points in order to fit best the log–log catalytic effectiveness curve.

Considerable film diffusion resistance. In

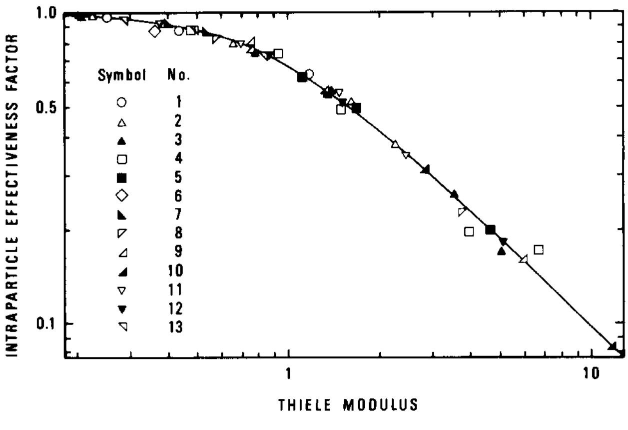

FIG. 1. Intraparticle catalytic effectiveness vs Thiele modulus. Experimental values, based on estimates of intrinsic properties in Table 1, are reported (numbers as in Table 1).

some operating conditions mass transfer resistance on the boundary layer outside catalyst particles is an important factor affecting overall reaction rate. This is certainly the case when observed reaction rate can be increased by increasing stirring speed.

No attempt has been given in the literature to mass transfer to dispersed solid particles in a dispersion of two liquid phases in agitated vessels. Available results for the case of a single liquid (*18*) are not necessarily useful in predicting behavior of triphase systems.

Since so many different factors could be important, the following treatment is to be considered only for comparison purposes and limited to the data obtained (*12–14*), with most experimental parameters kept constant. Since catalyst grains meet dispersed organic drops only intermittently, we shall consider an average mass transfer coefficient k_L for component A between the organic phase and the particle surface. The molar rate of depletion of component A from organic phase will be

$$-\frac{dN_A}{dt} = S_x k_L (C_A - C_{As}) V_{cat} \qquad (7)$$

At steady state molar rates given by Eq. (1) and by Eq. (7) coincide and, eliminating the concentration at particle surface C_{As}, the overall reaction rate for a unit volume of organic phase is

$$-\frac{dC_A}{dt} = \left[\frac{RV_{org}}{3V_{cat}k_L} + \frac{V_{org}}{k\lambda M_c \eta}\right]^{-1} C_A \qquad (8)$$

The reciprocal observed rate constant

$$\frac{1}{k_{obs}} = \frac{RV_{org}}{3V_{cat}k_L} + \frac{V_{org}}{k\lambda M_c \eta} \qquad (9)$$

is made up of the sum of two resistances in series, the former due to film diffusion and the latter due to both intrinsic reactivity and particle diffusion. As apparent reaction rate in the absence of film diffusion is available from experiments, Eq. (9) allows k_L to be evaluated. This procedure obviously will fail when film diffusion resistance is as low as the experimental error in the reciprocal of the observed rate constants.

Introducing the Biot number, $\mathrm{Bi} = k_L R/(3D_s)$, the overall catalytic effectiveness, which takes into account film resistance as well as intraparticle diffusion, may be given in the standard form

$$\eta_0 = \frac{\eta}{1 + \omega^2/\mathrm{Bi}} \qquad (10)$$

where η is still given by Eq. (3).

RESULTS AND DISCUSSION

Negligible Film Diffusion Resistance

Observed rate constants were measured (*12–14*) at different stirring speeds up to limiting values which were not affected by further increasing the stirring speed. The plateau values were maxima for the considered particle size and could not be increased using some other efficient methods of mixing, such as vibromixing and ultrasonic mixing. We assumed in our analysis that film resistances were negligible when

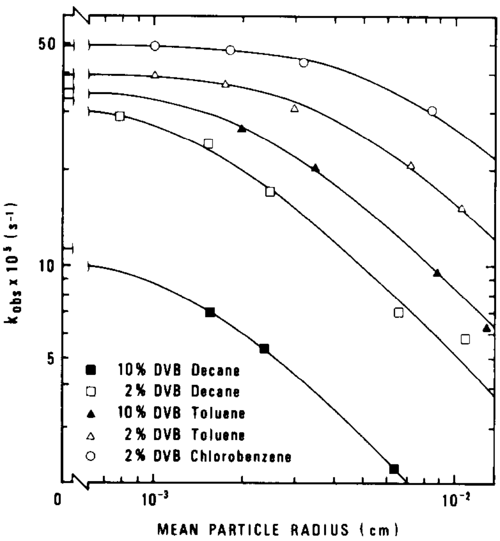

FIG. 2. Log–log plot of apparent reaction rate constants vs mean particle radius. Solid lines are calculated accordingly with Eq. (5′) and estimates of intrinsic properties in Table 1. Reaction of 1-bromooctane and aqueous NaCN with polystyrene-supported benzyltri-n-butylphosphonium salt as phase-transfer catalyst.

TABLE 1

Effective Diffusivities of Organic Substrates Within Catalyst Particles, D_s, and Products of Intrinsic Reaction Rate Constant and Partition Coefficient, $k\lambda$, Estimated from Data by Tomoi and Ford (*12–14*) at 90°C

No.	$D_s \times 10^8$ ($cm^2\ s^{-1}$)	$k\lambda$ ($cm^3\ mol^{-1}\ s^{-1}$)	Reaction[a]	Catalyst[b]	%DVB	Solvent	Swelling solvent	Power[c] water
1	55	29	1	1	2	Chlorobenzene	3.0	1.8
2	13	24	1	1	2	Toluene	2.2	1.8
3	2.2	21	1	1	10	Toluene	1.4	1.0
4	0.65	20	1	1	2	Decane	1.0	1.8
5	0.15	6.6	1	1	10	Decane	1.0[d]	1.0
6	48[e]	1.1[e]	1	2	2	Chlorobenzene	3.0	2.0
7	1.6	1.1	1	2	10	Toluene	1.4	1.0
8	0.14[e]	0.96[e]	1	2	2	Decane	1.0[d]	2.0
9	20	440	2	1	2	Toluene	2.2	1.8
10	2.7[e]	360[e]	2	1	10	Toluene	1.4	1.8
11	23	37	2	2	2	Toluene	1.6	2.0
12	3.1	37	2	2	10	Toluene	1.4	1.0
13	3.4	11	3	1	2	Toluene	2.2	1.8

[a] Reaction 1: $n\text{-}C_8H_{17}Br + NaCN\ (aq) \rightarrow n\text{-}C_8H_{17}CH + NaBr\ (aq)$. Reaction 2: $C_6H_5CH_2Br + NaCN\ (aq) \rightarrow C_6H_5CH_2CN + NaBr\ (aq)$. Reaction 3: $n\text{-}C_{16}H_{33}Br + NaCN\ (aq) \rightarrow n\text{-}C_{16}H_{33}CN + NaBr\ (aq)$.

[b] Catalyst 1: polystyrene-supported benzyltri-n-butylphosphonium salt. Catalyst 2: polystyrene-supported benzyltrimethylammonium salt.

[c] Swollen volume/dry volume of catalyst at 25°C.

[d] Estimated.

[e] Estimates obtained from data of two particle sizes only.

plateau values were reached. For each set of experimental data obtained at plateau values with respect to stirring rate and at different particle sizes, the log–log plot of observed apparent reaction rate constants, k_{obs}, vs mean particle radius, R, were considered. (This is equivalent to a plot $k_{obs}V_{org}/M_c$ vs $(R/3)\sqrt{M_c/V_{cat}}$ for our purposes, since M_c, V_{org}, and V_{cat} were kept constant in each set of data.) These plots are reported in Fig. 2 for the reaction of 1-bromooctane and aqueous sodium cyanide in different solvents with polystyrene-bound benzyltri-*n*-butylphosphonium salt as catalyst. Translated rows of experimental points are in Fig. 1. Estimates of products $k\lambda$ and effective diffusivities D_s were derived as discussed before. Theoretical solid lines in Fig. 2 were obtained from Eq. (5′) using estimated $k\lambda$ and D_s.

In Table 1 estimates of $k\lambda$ and D_s are given for all sets of experimental data presented by Tomoi and Ford. In Figs. 3–6 apparent rate constants and theoretical predictions (solid lines) are reported vs reciprocal radius of catalyst particles. In Fig. 7 experimental and predicted values are compared: more than 90% of the measured rate constants lie within the range ±10% of the calculated values.

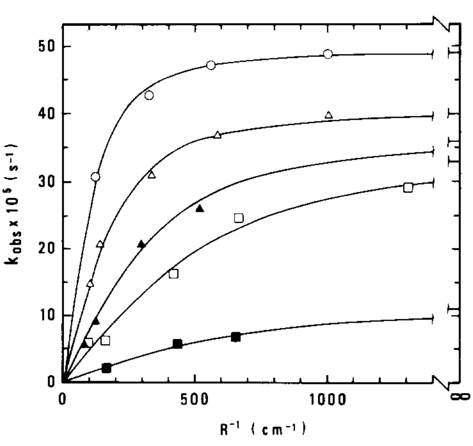

FIG. 3. Apparent reaction rate constants vs reciprocal mean particle radius. All conditions are the same as in Fig. 2. A useful comparison can be made with the equivalent Fig. 5 in Ref. (*13*).

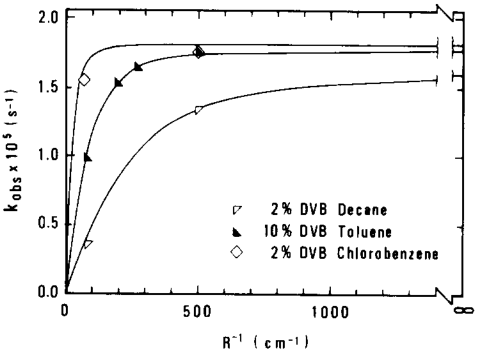

FIG. 4. Apparent reaction rate constants vs reciprocal mean particle radius. Reaction of 1-bromooctane and aqueous NaCN with polystyrene-supported benzyltrimethylammonium salt as phase-transfer catalyst.

Although, due to the limited number of available experimental data, estimates in Table 1 are to be regarded mainly as orders of magnitude, a few comments on how these results agree with physical operating conditions can be made. Effective diffusivity within the catalyst particle correctly decreases by decreasing the swelling power of the solvent and increasing the degree of crosslinking of the polymeric support. In addition it is fairly independent on the specific reaction and the nature of active sites.

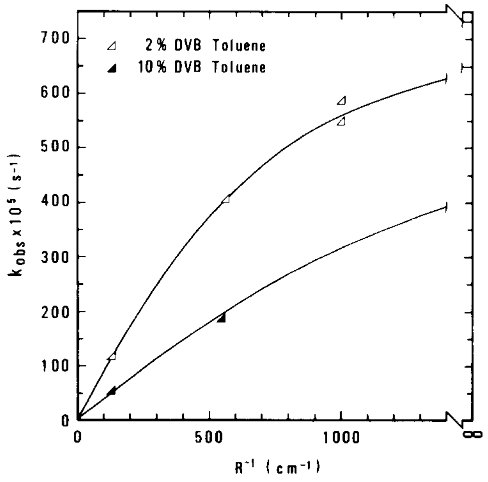

FIG. 5. Apparent reaction rate constants vs reciprocal mean particle radius. Reaction of benzyl bromide and aqueous NaCN with polystyrene-supported benzyltri-n-butylphosphonium salt as phase-transfer catalyst.

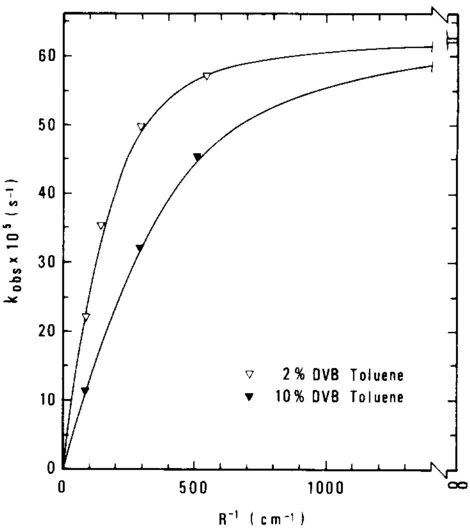

FIG. 6. Apparent reaction rate constants vs reciprocal mean particle radius. Reaction of benzyl bromide and aqueous NaCN with polystyrene-supported benzyltrimethylammonium salt as phase-transfer catalyst.

Also, orders of magnitude of D_S are as reported in the literature for comparable conditions (*9*).

Moreover, looking at the product $k\lambda$, we notice that for a given solvent it seems to decrease slightly whenever the degree of crosslinking of the polymer increases, which is in good agreement with tighter limitations on the transition state or with low-

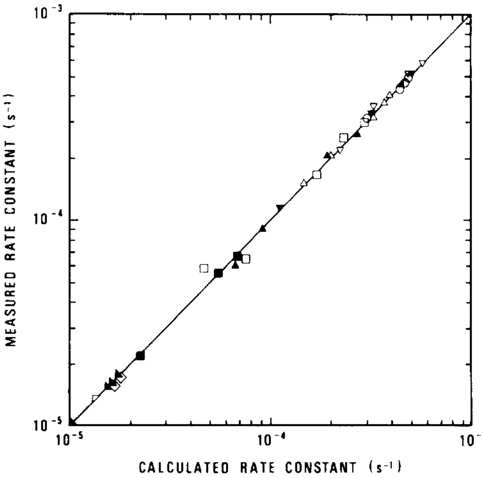

FIG. 7. Comparison between experimental apparent rate constants and calculated values using estimates of intrinsic properties in Table 1.

ering of the steric factor as discussed previously.

Considerable Film Diffusion Resistance

At stirring rates less than 600–650 rpm using the polymer-supported quaternary phosphonium ion, and at less that about 400 rpm using the less active polymer-supported quaternary ammonium ion catalyst, film diffusion resistance was important (*12–14*). Rather different limiting stirring speeds were reported by others (*10–11*), depending on the particular experimental apparatus adopted and on how active the catalyst was.

Data presented by Tomoi and Ford were examined by the previously discussed procedure. Two particle sizes (−60+100) and −100+200 mesh on dry polymer basis), with toluene as solvent and benzyltri-n-butylphosphonium ions supported on polystyrene at different degrees of crosslinking as phase-transfer catalyst, were considered.

Obtained average mass transfer coefficients are reported in Fig. 8. These results, as was pointed out before, are to be considered strongly dependent on the specific experimental apparatus and should be used very cautiously for practical scaling purposes to different situations. We may expect, however, that mass transfer coefficients through the boundary layer outside the particle do not depend on inner properties of the catalyst, as intrinsic reactivity or degree of crosslinking of polymeric support (though the degree of crosslinking may have some influence as it affects swelling and therefore the actual radius of the swollen particle). From a comparison of the two considered particle sizes, mass transfer coefficients for larger particles seem to increase quickly by increasing the stirring rate. On the contrary smaller particles exhibit a higher mass transfer coefficient at moderately low stirring rates which is not so sensitive, however, to increasing stirring speed.

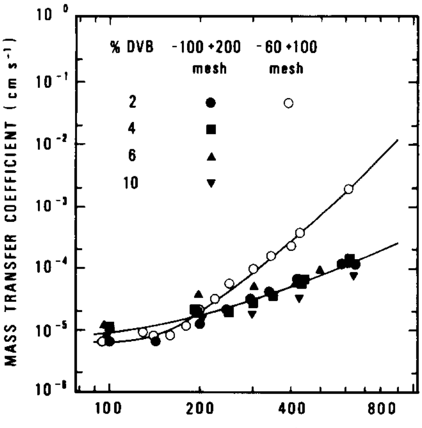

FIG. 8. Experimental average mass transfer coefficient vs stirring speed for two particle sizes (−60+100 and −100+200 mesh on dry basis). Toluene as solvent.

APPENDIX: NOMENCLATURE

Bi	Biot number, dimensionless
C_A	concentration of species A, mol cm^{-3}
C_{As}	concentration of species A at surface of catalyst particles, mol cm^{-3}
D_s	effective diffusivity within catalyst particles, cm^2 s^{-1}
k	intrinsic reaction rate constant, cm^3 mol^{-1} s^{-1}
k_L	mass transfer coefficient based on unit exterior surface of particle, cm s^{-1}
k_{obs}	apparent reaction rate constant, s^{-1}
M_c	molar equivalents of catalyst, mol
N_A	moles of species A, mol
R	radius of swollen catalyst particles, cm
S	error sum of squares
S_x	exterior surface of particles per unit volume of catalyst, cm^{-1}
t	time, s
V_{cat}	volume of swollen catalyst, cm^3
V_{org}	volume of organic phase, cm^3
η	intraparticle catalytic effectiveness, dimensionless
η_0	overall catalytic effectiveness (including film diffusion resistances), dimensionless
λ	partition coefficient, dimensionless
ω	Thiele modulus, dimensionless

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